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FINAL REPORT

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**In-Plant Testing of Membranes
To Treat Electroplating Wastewater**

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BACKGROUND

This is the final report submitted for the work performed under the NASA Cooperative Agreement NCC3-301 for the project entitled "In-Plant Testing of Membranes To Treat Electroplating Wastewater". The project was initiated April 1, 1993 and was to have been completed by October 8, 1993.^{*} The funding level initially was set at \$38,230. A no-cost extension was requested and granted until April 8, 1994. A supplement of \$15,605 was awarded to continue the work through November 7.

The main objective of the research project was to determine if the crosslinked polyacrylic acid salt films developed by NASA scientists could be used for heavy metal removal from the wastewater generated by the metals-finishing or electroplating industry. A variety of tasks identified in the original proposal were completed. These included: 1) analysis of our industrial partner Aetna Plating's zinc electroplating process and its wastewater treatment needs for zinc removal, 2) design and construction of a laboratory-scale unit to continuously supply and remove the ion exchange films from the zinc wastewater, 3) performance of a series of runs on such a unit to determine its operating characteristics, and 4) design of a prototype unit for use at the industrial site. In addition, there were a number of tasks that had not been identified in the original proposal but were later judged to be necessary for the successful completion of the project. These were: 1) batch equilibrium and kinetic experiments with analysis of the experimental results to accurately determine the equilibrium and kinetic parameters for the ion exchange films, 2) simulation studies for proper design of the prototype unit, and 3) preliminary runs to exchange the films from H form to Calcium form. Since significant effort was expended in performing many of the

tasks that were not included in the original proposal, supplementary funding to complete the project was sought and granted.

Monthly progress reports were submitted for April, May, June, July, and August, 1993. Another progress report was submitted on October 30, 1993 for the activities during September and October 1993. Finally, another report was issued on January 27, 1994 covering activities for the months of November and December 1993, and January, 1994. These reports summarized the activities performed under the original funding.

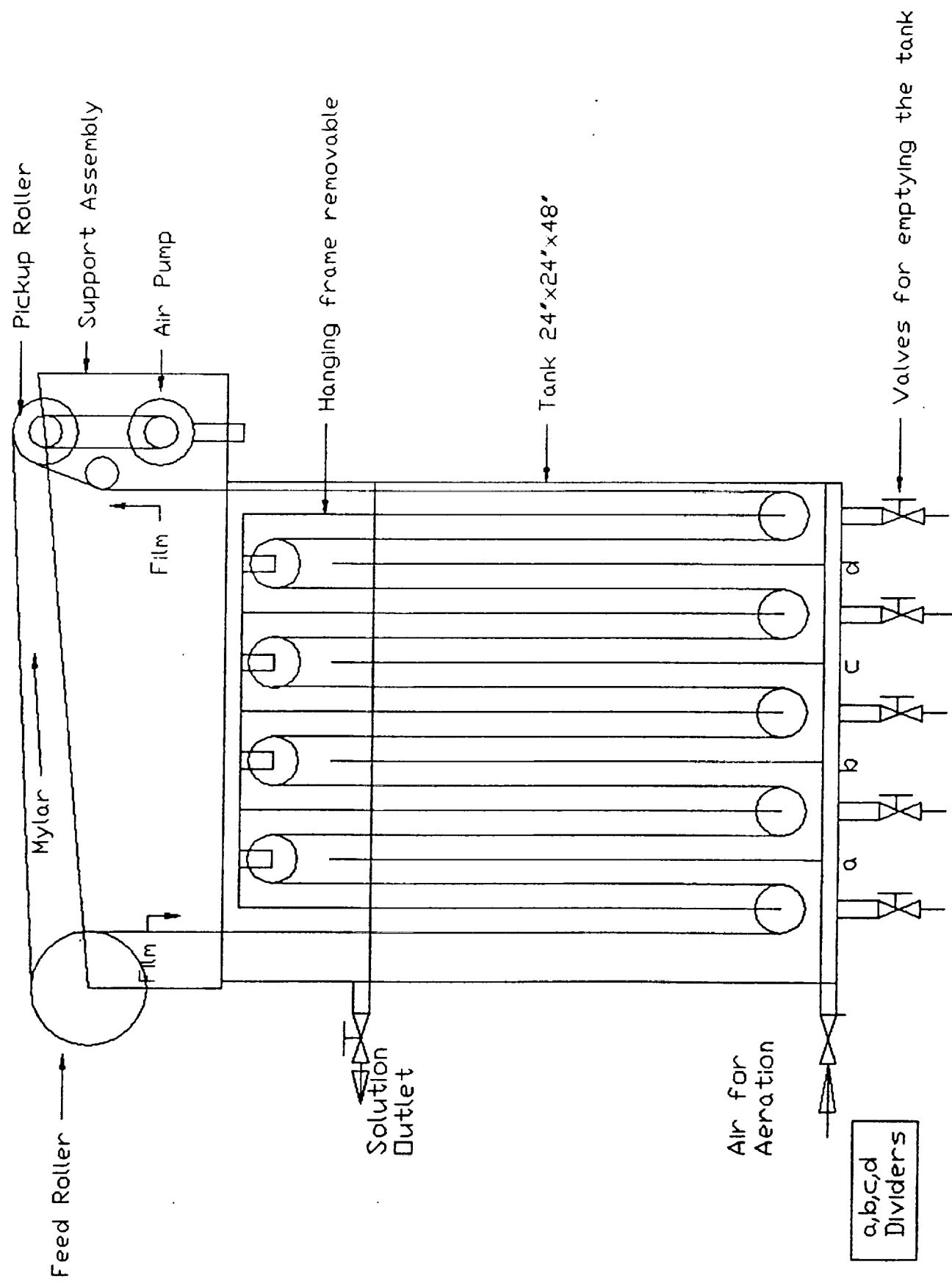
The supplementary funding was appropriated to complete the following tasks:

1) assembly and performance evaluation of the prototype, 2) oversee the production of 2,000 ft of ion exchange film, 3) conversion of the film to Calcium form, 4) preliminary runs with Ca-exchanged films in the laboratory-scale unit, 5) development of an experimental plan for tests at Aetna Plating, and 6) performing final tests at Aetna Plating. This final report details the activities related to the project performed by the Principal Investigator (PI) Dr. D.B. Shah and the Co-PI Dr. Orhan Talu during the last year.

1. ASSEMBLY AND PERFORMANCE EVALUATION OF THE PROTOTYPE

The design and the schematics of the prototype unit are shown in Figure 1. The design of the prototype unit was based on the simulation studies outlined in the last report. The prototype moved the film from the feed roller to the film uptake roller through a series of five tanks. The solution was moved in a direction opposite to the direction of film movement. This design feature was deemed necessary to achieve as high a loading of zinc on the film as is possible since a continuous mass transfer operation works most efficiently in a countercurrent mode of operation. The prototype unit was made of two parts: a tank with

Figure 1. Schematics of the Prototype



dividers attached to the walls of the tank to divide the tank into five compartments and a removable frame with five partitions and nine rollers. A high density polyethylene tank of 24"x24" cross-sectional area and 48" deep was divided into five separate sections by using four PVC dividers. The dividers were placed between two angles that were glued to the tank walls. Screws were used to fasten the dividers to the angles. To ensure that there was as little exchange of flows between the adjoining tanks as possible, a plastic sheet was laid at the bottom of the tank and the dividers were pressed firmly against the sheet. This arrangement resulted in five sections four of which were nearly of equal size and the fifth one was larger by about 50%.

The film was moved through the assembly by nine rollers. All nine rollers were fastened to the removable frame. Five rollers were fastened to the bottom of the five partitions and four rollers were fastened to the top of the frame. The frame could be placed on top of the tank so that each one of the five hanging partitions would be placed in the middle of each of the five tanks as shown in the figure. Before the experiment was started, the film was guided through the nine rollers on the frame and then the frame was inserted into the tank. Once the frame is properly placed in the tank, there is no way to guide the film through the different sections and over the nine rollers. The feed and pickup roller were supported on the opposite ends of a support frame which could be placed on top of the frame.

The roller assembly was driven by a variable speed air pump that was mounted on the support frame. The air pump was used to drive the pickup roller which, in turn, would drive each of the rollers and, ultimately, the feed roller. The speed of the pump could be

controlled so as to move the film through the prototype unit at a rate of approximately 1 ft/min. The tank was also provided with aeration mechanism. Two bubblers with equally spaced holes were placed at the bottom of the tank running along the length of the tank. Each of the tanks could be aerated, thereby, providing good mixing in each tank. These bubblers also served to drain the solution from the tank. All parts were made of plastic as metal parts were judged to be inappropriate as they could interfere with the electroplating operation of our industrial partner.

Important Considerations

Guide Belt: Is it Necessary? Since the film is being moved through the assembly by nine rollers that are fitted in a highly restricted space, a major problem is likely to arise if for any reason the film breaks or tears in the tank during the operation. There would not be any way to guide the film through and resume the operation without taking the whole assembly apart. The operation will have to be stopped. The tank will have to be emptied and the support assembly will have to be removed. The hanging frame will have to be removed and then the film could be guided through the rollers again. One way to overcome this problem is to have a guide belt in the system that continues to move over the nine rollers in a closed loop. Then, even if the film breaks, the film can be attached to the guide belt. And, by running the guide belt through the assembly, we can wind the film all the way through to the pickup roller. We tried window wire-mesh as a guide belt. However, our attempts to find a suitable means to attach the film to the mesh were not successful. Our clearance at the bottom was too small and paper clips or any other such means that we used failed to consistently guide the film all the way through. After considerable efforts, we gave

up on the idea of using a guide belt. Moreover, we also wanted to ensure that no parts or accessories made out of metal would fall into the tank. We decided to take a chance that the film would not break during the operation.

Without the use of a guide belt, the film was found to stick to the smooth PVC surfaces of rollers, dividers and partitions thereby significantly increasing the resistance to rolling. The pump power was then not enough to rotate the rollers and the film would stop moving. To overcome this problem, each of the dividers and rollers was individually covered with the wire mesh. As a result, the film did not directly come in contact with the smooth PVC surface. This arrangement appeared to work quite well.

Bottom Rollers Off-Centered In spite of the original design specification that the bottom rollers be placed exactly in the center of the hanging partitions, the assembly constructed had the rollers in off-centered positions. As a result, the clearance on one side between the film and the dividers was quite small and in many instances, the film stuck to the dividers or the wire mesh. This limited the accessibility of one side of the film to the solution thereby decreasing the removal efficiency. We were unable to rectify this problem as correcting it would have required building a completely new frame.

2. OVERSEEING THE PRODUCTION OF ION-EXCHANGE FILMS

Chemsultants International of Mentor, Ohio, was awarded the contract of making the film for use at Aetna Plating. A roll of film was prepared by Chemsultants using Mylar as the base material and a wire mesh. The film was much thinner than the one we had obtained from Baldwin-Wallace and did not appear to have mechanical strength in X and Y directions. the film needs to possess the necessary mechanical strength to roll through the tank assembly

twice: once for the calcium conversion process and secondly for the removal of zinc from the solution. Preliminary experiments were performed with a small piece of this film. The film was put in a solution of calcium salt to check for its calcium conversion properties. The film experienced severe flaking problems. It was clear that the film could not be used for our purpose. The adhesion between mylar, the film and the wire-mesh was poor. Mylar appeared to be inappropriate as a base support material for our application.

The Principal Investigators (Drs. D.B. Shah and Orhan Talu) visited the Chemsultants' facilities in Mentor, Ohio on May 27, 1994 to observe first hand their apparatus and operational procedures. We wanted to familiarize ourselves with their film fabrication facilities and to offer our input in improving the quality of the film. We offered a specific suggestion of bringing in mesh and mylar together and then spraying the ion-exchange film solution on to the mesh and mylar. Such a setup might provide a better adhesion between the film and the base. A copy of the memo is attached herewith.

Evaluation of Binding Between Support and the Film

The original mesh selection was based on convenience rather than a result of any specific investigation. The film solution appeared to encapsulate the mesh and the adhesion appeared satisfactory. However, a mesh material which was wetted by the film solution would provide a better adhesion rather than just encapsulate the mesh. If the film just encapsulates the mesh, it may fall off the support if the film is chipped. Chemsultants, with input from Dr. Phillip from NASA and Dr. Thomas from Bionetics, investigated several support materials such as Reemay (style 2006 polyester [phthalic anhydride]), Lydall syntra 5007-AX, sonatra 8017, sonatra 8411 and dura glass. In all, we were supplied with 14

samples of coated mesh. We evaluated these samples for the quality of binding between the support and film. Three approaches were used in evaluating this binding: 1) optical transmission micrography, 2) scanning electron microscopy, and 3) desk-top wetting observations. Optical micrographs proved to be inconclusive in determining the film adhesion to the support. The scanning electron micrographs were extremely useful in identifying the contact angle between the film and the support material. Large contact angles are indicative of good degree of surface wetting. The desk-top experiments were performed during the meeting at Bionetics on July 8, 1994. These experiments involved placing a drop of film solution directly on a sheet of support material. The soaking speed of the film solution and the contact angle of the drop with the support is indicative of wetting. We examined 14 samples. These were:

- 1) the "old" fly mesh coated with film, (this was used during all experiments at CSU)
- 2) Reemay Style 2006 - polyester (phthalic anhydride)
- 3) Lydall 15#Syntra 5007 - AX - polyester + rayon
- 4) Sonatra 8017 - polyester (phthalic anhydride)
- 5) Sonatra 8411 - polyester (phthalic anhydride)
- 6) Dura Glass - film in acid form, 8g/100g glutaraldehyde/PVA
- 7) Dura Glass - film in Ca form, 3g/100g glutaraldehyde/PVA
- 8) Dura Glass - film in acid form, 3g/100g glutaraldehyde/PVA
- 9) Chemsultants poly - film Ca form from 400 ft roll
- 10) Chemsultants poly - film acid form, 3g/100g glutaraldehyde/PVA
- 11) Chemsultants poly - film Ca form, 3g/100g glutaraldehyde/PVA

- 12) Chemsultants poly - film Ca form, 5g/100g glutaraldehyde/PVA
- 13) Chemsultants poly - film acid form, 8g/100g glutaraldehyde/PVA
- 14) Chemsultants poly - film H form from 400 ft roll

The film samples and their representative scanning electron micrographs are attached in the appendix. The old fly mesh screen showed no adhesion. The resulting film is thick because the material is coated thick resulting in good encapsulation. The film did not wet the Reemay and Lydall supports (samples 2 and 3). Good adhesion (a large contact angle) was observed for samples 4 and 5 with sample 5 being better. The scanning electron micrographs of samples 6 through 14 showed no variation with the amount of the cross-linking agent or the nature of the film (H or Ca form). The film solution did not wet the Chemsultants polyethylene mesh (samples 9-14). The wetting on Dura Glass was very good (samples 6-8) and comparable to sonatra material. The two best candidates for the support materials were narrowed down to Sonatra 8411 and Dura Glass. Table-top wetting experiments showed that the film solution "infiltrates" Dura Glass faster than Sonatra 8411. This is an important consideration since there is a short time interval (about a minute) in the coating process before the film sees high temperature and cross-links. No infiltration can occur once the film is cross-linked. The disadvantage of Dura Glass is its weakness when "pinched" and the glass fibers break. Sonatra 8411 did not have the pinching problem but the rate of infiltration is much slower. This could be overcome by rolling the film slower or increasing the rate of infiltration by conducting the process at higher pressure. Dura Glass was preferable if pinching of the film can be avoided. Finally, Dura Glass was chosen as the support material with a view towards trying out a 400-ft roll of film on Dura Glass on the

prototype built at AMC. This material proved to be a good choice as a support as Chemsultants produced three 1000-ft rolls with Dura Glass and Mylar as the support materials. This film appeared to possess the necessary strength and was used to perform many of the preliminary experiments outlined earlier to debug the prototype.

3. CONVERSION FROM H-FORM TO CALCIUM FORM

The film is most effective in removing zinc from solution in the Calcium form rather than the H-form that it is manufactured in. The film, therefore, had to be ion-exchanged to Ca-form by treating it with a calcium salt solution. The chemistry and the optimum conditions under which this ion-exchange process is to occur were determined by Dr. Street in his laboratories at NASA. Schematics of the experimental setup used to perform the conversion process are illustrated in Figure 2. There are two tanks: one is a reservoir tank of approximately 57 liter volume and is placed on the table-top at an elevation of 4 ft, and the other is a conversion tank of about 34 liter volume and is placed on the floor. The solution in the two tanks is continuously circulated between the two in a closed loop fashion. The solution from the conversion tank is pumped into the reservoir tank by a submersible pump that is placed in the conversion tank. The pumping rate is controlled by means of a valve to about 1.8 lit/min. The overflow from the reservoir tank is gravity fed back into the conversion tank. The contents of the reservoir tank were mixed with a variable speed mixer. The pH of the solutions in conversion and reservoir tanks is monitored by means of a pH meter. A bubbler made out of pyrex is placed in the conversion tank and an in-house air supply is used to aerate the solution to achieve mixing in the tank. The air was cleaned of grease and other particulate matter by passing through a filter.

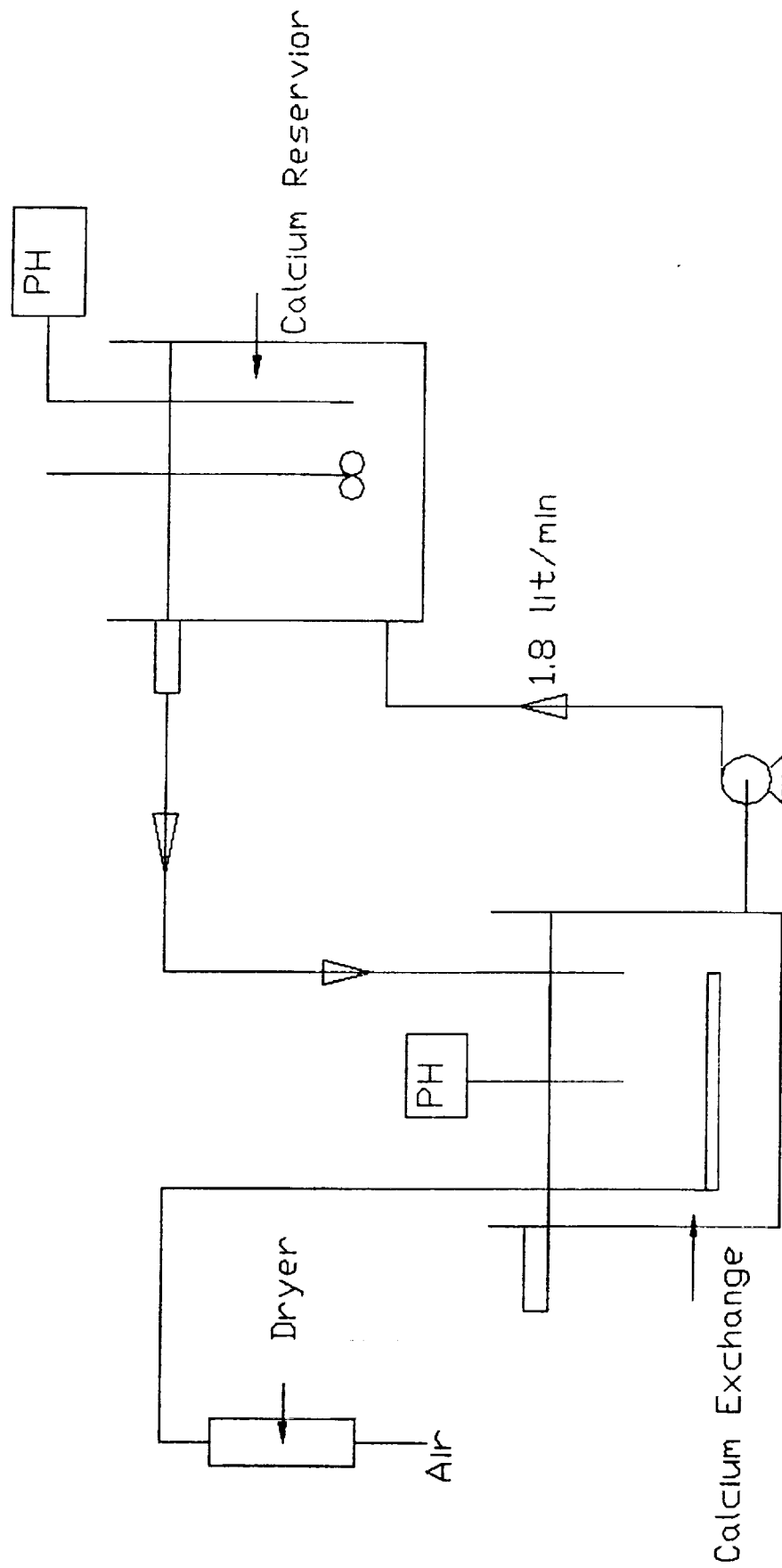


Figure 2. Experimental Setup for H-Ca Exchange

For Calcium conversion, only the removable frame described above was used and not the tank. Moreover, according to procedure outlined by Dr. Street, the contact time between the film and the conversion solution had to be on the order of one minute. Hence, all nine rollers on the frame were not used. Two guide rollers were placed on the support frame that carried the air pump and the film was wound over only one central bottom roller. The schematics are shown in Figure 3. The speed of the variable air-pump was adjusted to move the film at a speed of about 1 ft/min. This resulted in the film having the residence time of about 1-1½ min. The frame was placed on a wooden support assembly (constructed by Drs. Street and Savino) and the conversion tank was placed underneath the frame. Two separate preliminary runs were performed. The main objectives of these preliminary experiments were to finalize the conditions under which the three rolls of 1000-ft film would be treated for Calcium conversion.

The first preliminary experiment was performed without the film to determine if the circulation rate between the two tanks was adequate and the time it took for the pH in the two tanks to equalize. Both tanks were filled with deionized water. The experiment was begun by adding a 1 ¼ liter of saturated $\text{Ca}(\text{OH})_2$ solution in the reservoir tank. The initial pH of the reservoir tank was 8.95 whereas that of the conversion tank was 7.5. The pH in both tanks was monitored as a function of time and the results are shown in Figure 4. After a period of about 45 minutes, the pH in the two tanks approached one another. This time is approximately equal to one residence time (91 liter/1.8 lit/min). The degree of mixing and the circulation rate were, therefore, judged to be appropriate.

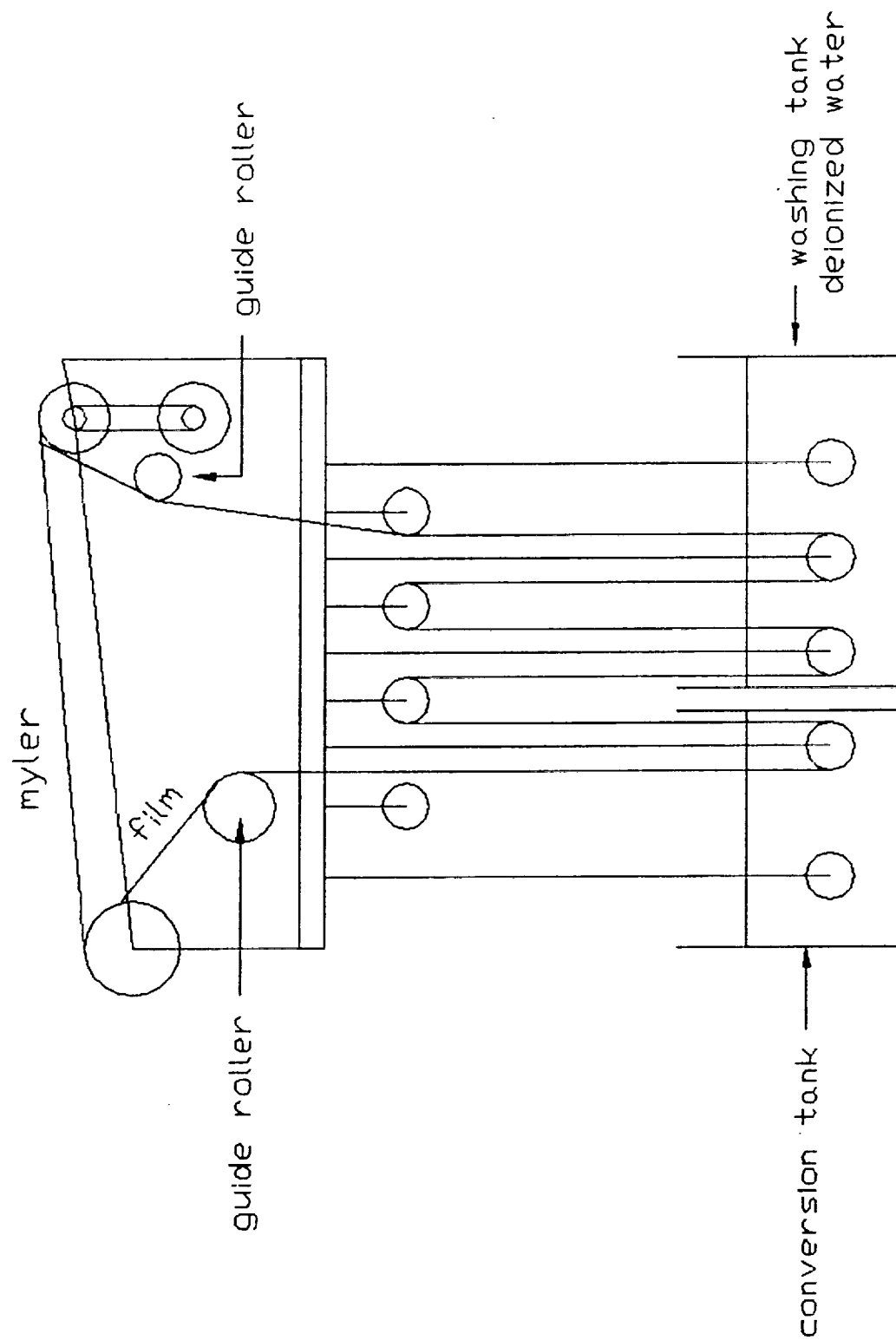


Figure 3. Schematics of Hydrogen Calcium Exchange

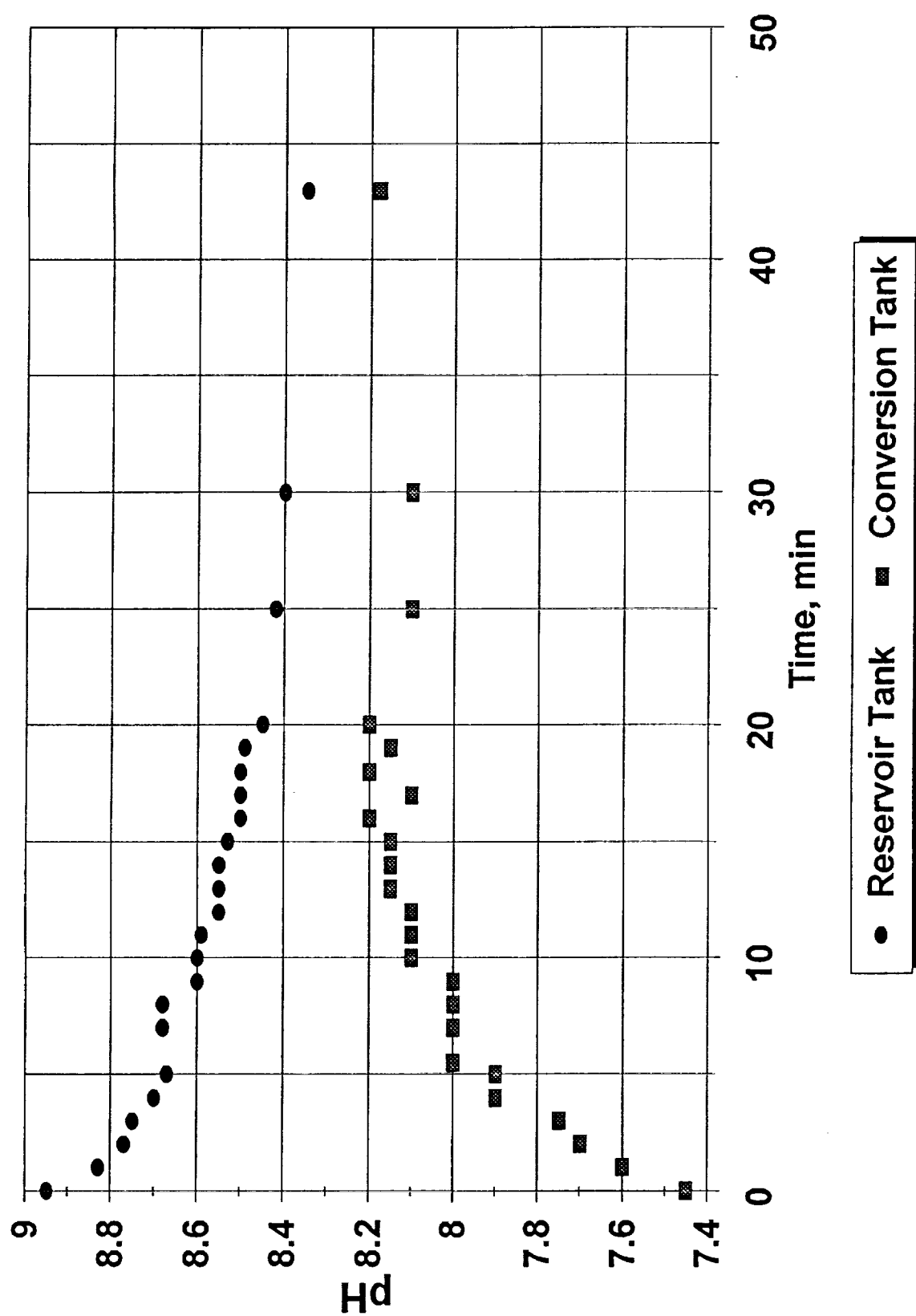


Figure 4. Variation of Reservoir and Conversion Tank pH with Time

In the second experiment, the initial strength of the $\text{Ca}(\text{OH})_2$ solution in the conversion tank was 0.008 mol/lit. The experiment was run for a period of about 2½ hours. During the process of H-Ca exchange, H^+ ions come into solution and the pH of the conversion tank decreases. To maintain the pH of the solution in 5-6 range, a spoon of calcium hydroxide and acetic acid were added to the reservoir tank periodically. The film speed was maintained at 1 ft/min. The experiment was continued for 2½ hours. The results are shown in Figures 5 and 6. Figure 5 shows the variation in the pH of reservoir and conversion tanks. There appears to be significant fluctuations in the pH of both tanks during the first 60 minutes but, for the rest of the experiment, the pH of the reservoir is reasonably constant at about 8.75 and that in the conversion tank at 7. Figure 6 also shows the times at which deionized water, acetic acid and scoop of $\text{Ca}(\text{OH})_2$ were added. The converted film roll was analyzed for the degree of calcium exchange. On an average, only 10% calcium exchange was achieved. This is much lower than the 70% conversion that is needed for the film to be used at Aetna.

It was later discovered that the starting concentration in the tank should be 0.08 rather than 0.008 that was used in the second experiment. The degree of calcium exchange as a function of starting molar concentration as determined in NASA laboratory is shown in Figure 7. To achieve a conversion of 50%, the starting concentration must be 0.12 mol/lit. A third experiment was performed on November 23, 1994, with a starting concentration in both tanks of 0.15 mol/lit. The results are shown in Figure 8. The pH in the reservoir tank averaged 8.2 while that in the conversion tank was 7.2. The figure also shows the times at which a scoop of $\text{Ca}(\text{OH})_2$ was added to the reservoir tank. The run was a success and later

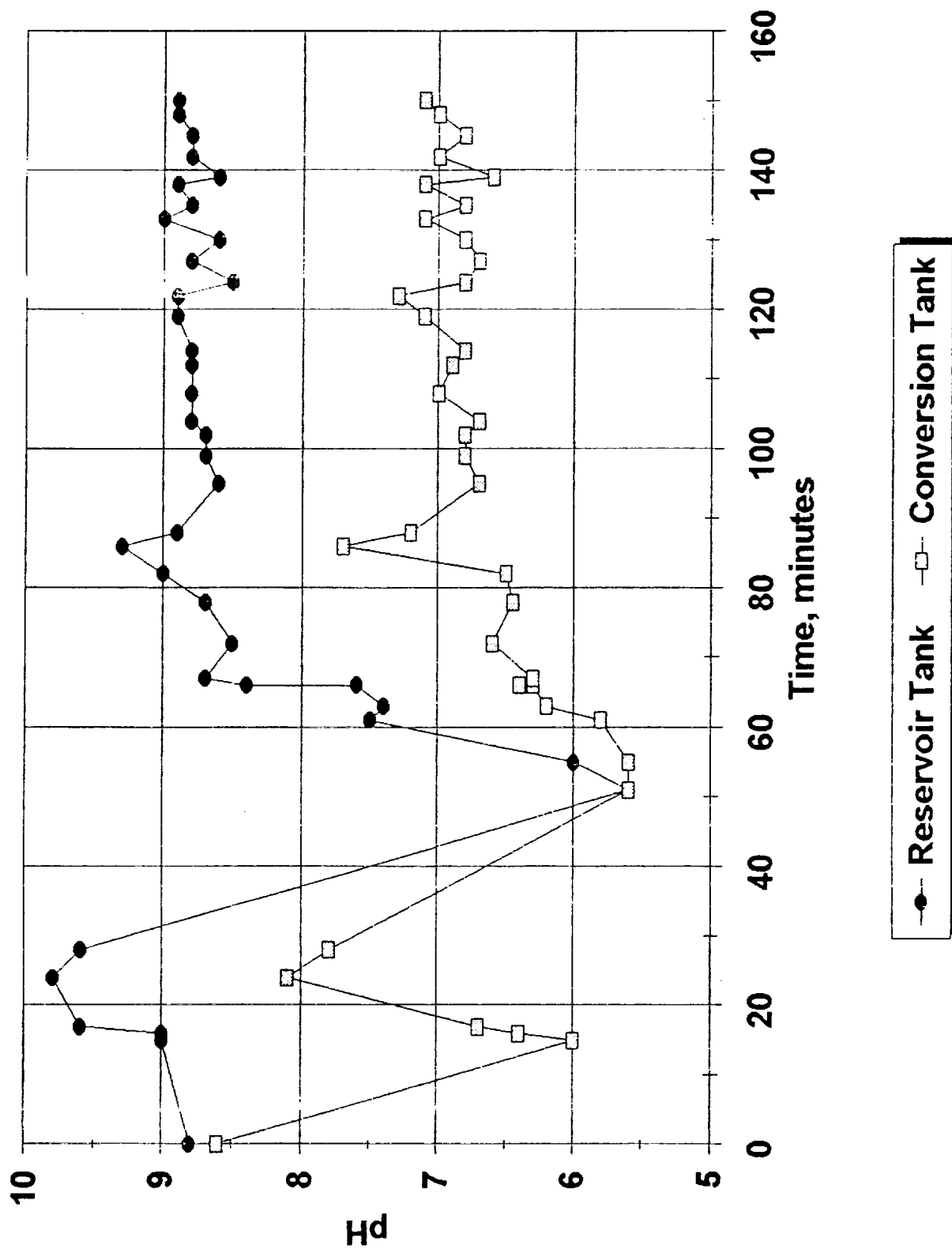


Figure 5. Variation of pH during Hydrogen Calcium Exchange

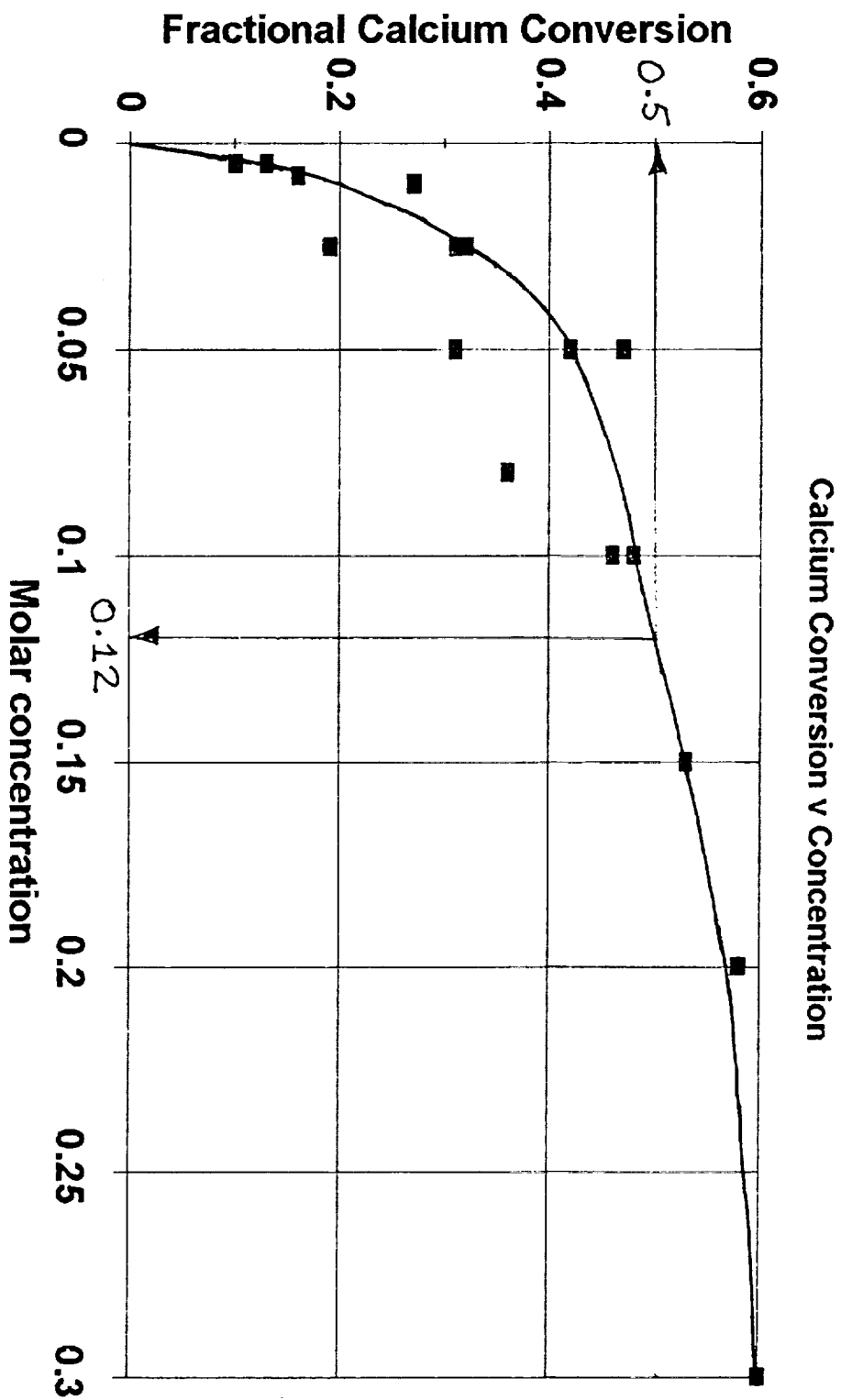


Figure 7. Degree of Hydrogen Calcium Exchange as a Function of Calcium Concentration

Calcium Conversion 11/23/94

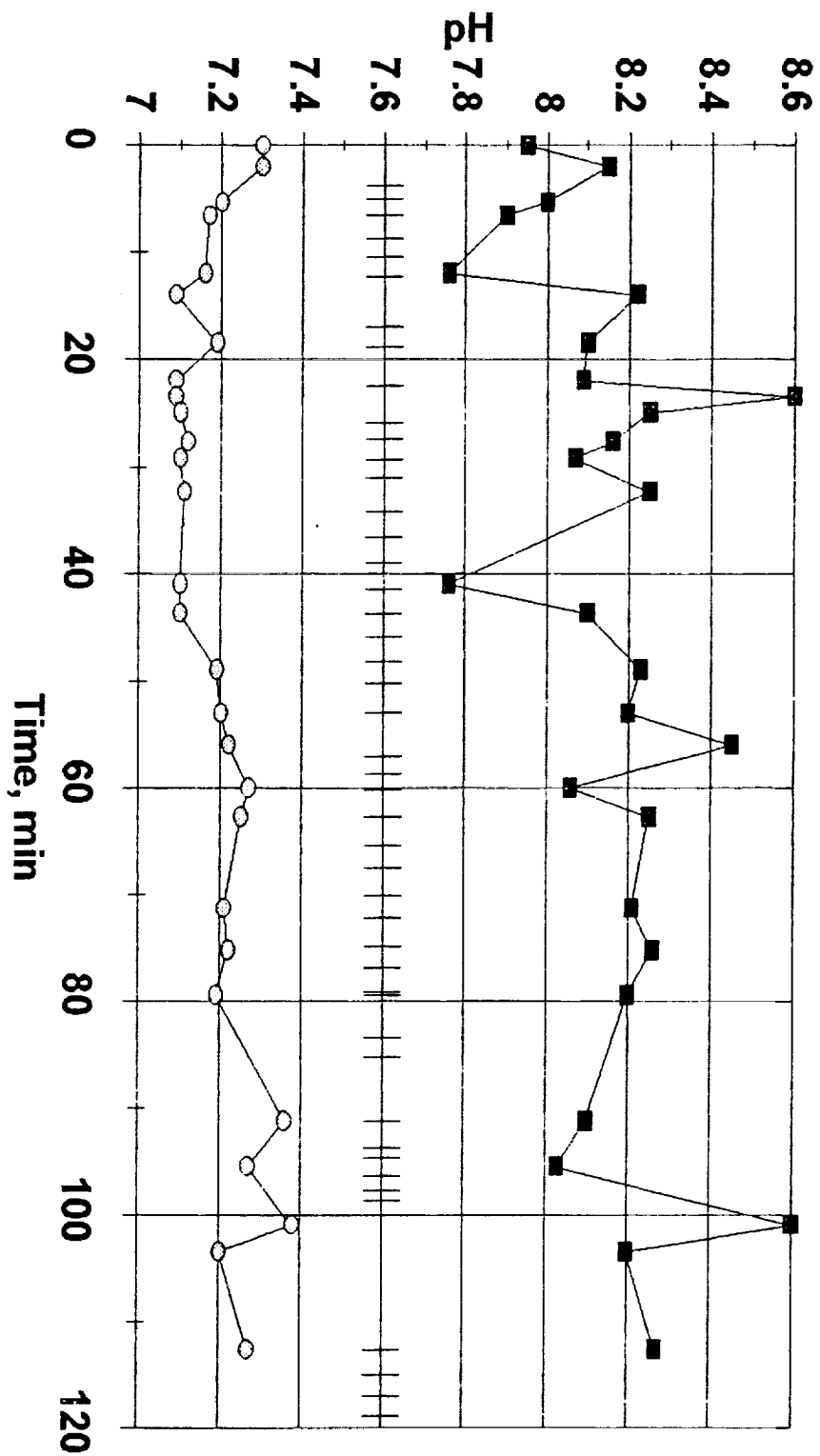


Figure 8. Experimental Protocol for Hydrogen Calcium Exchange

analysis of the converted film indicated that on an average 50% calcium conversion was achieved. Based on the results of the third experiment, we felt confident that we had identified operating conditions under which the H-Ca exchange could be successfully performed. It was decided that before the 3000-ft film was calcium exchanged, the calcium exchanged film of about 150 ft should be run through the prototype to check the operation of the prototype and the performance of the film.

4. PRELIMINARY EXPERIMENT WITH Ca-EXCHANGED FILM IN PROTOTYPE

The zinc test was performed on December 8, 1994. It was decided to perform the test with the zinc solution in a batch mode rather than the continuous mode in which the test would be carried out at Aetna Plating. Circulating the solution continuously through the tank for a period of three hours posed a number of problems such as, 1) the time period for the experiment (at the most 2½ hours) not being long enough to achieve the steady-state, 2) the disposal problem associated with the zinc solution, etc. How to start the experiment was also a concern. Since the film had to be wound around the rollers before the frame is placed in the tank, a 40-ft film was used up leaving only about 150-ft film available for the zinc uptake experiment. Since some time delay is involved before the experiment is started, the film in contact with the solution immediately starts exchanging the zinc. This exchange had to be accounted for in the data analysis. One could use the mylar as the lead in for the film but this required finding a way to attach the film on to the mylar. Since our experience with using a guide belt was unfavorable, we did not use the mylar as a lead in.

The experiment was started with the air pump moving the film through at the rate of 1 ft/min. The experiment failed as the film, after passing through a couple of rollers,

encountered significant resistance to the motion. After a while, the resistance increased to such an extent that the rollers stopped rotating and the film was torn. Once the film is torn, there is no way to restart the experiment without stopping the experiment and rewinding the film over the rollers outside the tank.

Problems

The main problem was the tearing of the film. It was suggested that the number of rollers over which the film is wound be decreased to reduce the stress on the film. Such a change in the design of the unit would necessitate dismantling the prototype as has been built. Also, some of the dividers and partitions may need to be removed. These changes are irreversible in nature and would necessitate redesigning and rebuilding the prototype unit.

Another problem we encountered during this run was the precipitation of the zinc from the solution. The pH of the zinc solution prepared was quite low (between 4 and 5). Since the film works best with the pH in the neutral range, we added $\text{Ca}(\text{OH})_2$ to the solution to increase its pH. But, as the pH increased, the zinc appeared to precipitate out.

CONCLUDING REMARKS

At this point of the project, it was clear that the prototype as was designed would not work satisfactorily. The film does not appear to be strong enough to run through the prototype twice (once for the H-Ca exchange and once for the zinc uptake) and the design of the prototype is not forgiving enough to tolerate any weakness in the film. The prototype had to be rebuilt with a different drive mechanism. Since no funds were available to completely rebuild the system, our colleagues at NASA decided to undertake the responsibility of rebuilding the prototype, evaluating its performance and field-testing it at

Aetna Plating. The PIs have agreed to provide any input and assistance sought by NASA during 1) the redesign and rebuilding of the prototype, 2) its performance evaluation, 3) development of a test plan at Aetna and 4) analysis of the data.

Appendix A

**Various Samples and Their
Scanning Electron Micrographs**

5006

Sample # 2

5007 AX

Sample # 3

8017

Sample # 4

8411

Sample # 5

Sample # 6

Sample # 7

Sample # 8

Sample # 9

Sample # 10

Sample # 12

Sample # 13

Sample # 14



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